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HIGH ENERGY THERMOPLASTIC ELASTOMER PROPELLANT

The invention described herein may be manufactured, used, and licensed by or for the U.S. Government for U.S. Governmental purposes.

FIELD OF THE INVENTION

The present invention relates generally to a high energy propellant composition. More particularly the invention relates to a propellant that includes an energetic thermoplastic elastomer as a binder and a high energy, high density filler.

BACKGROUND OF THE INVENTION

As with the evolution of many technologies, new weapon systems require higher munitions performance. Current standard propellants do not have adequate energy to deliver the performance required for systems that are presently being developed. JA2, which is a standard double base propellant used, for example, in the M829A1 and M829A2 tanks rounds, has an impetus value of 1150 Joules/gram or J/g. M43, which is used in the M900A1 cartridge, has an impetus of 1181 J/g. Both of these conventional propellants do not have the energy level to deliver the muzzle velocity required in future high energy tank systems such as the M829E3. Theoretical calculations have shown that a propellant containing an energy above the 1300 J/g threshold is needed.

In addition to the energy content, it has been shown by theoretical calculations that the ballistic cycle can be optimized and work output can be maximized by using a combination of two equienergetic propellants whose burning rates are different by a factor of three or four. The slow burning propellant is designed to enter the cycle at a later time. Current standard propellants do not exhibit such wide variation in burning rates at a specified energy level. Standard tank gun propellants such as XM39, M43, M44 or JA2 have burning rate differentials that are, at best, less than two to one, and thus they are unsatisfactory for solving the problem of delivering much higher muzzle velocities.

In addition to the inability to generate adequate energy levels, present day propellants produce volatile organic compounds and ancillary waste, especially in enhanced demil and recyclability.

Accordingly, one object of the present invention is to provide a pair of high energy propellants whose average impetus is at or above the 1300 J/g level.

Another object of this invention is to provide a pair of high energy propellants whose burning rate differential is three or greater.

An additional object of this invention is to provide new energetic materials and processes that eliminate or greatly reduce both volatile organic compound production and ancillary waste through demil and recyclability.

Other objects will appear hereinafter.

SUMMARY OF THE INVENTION

It has now been discovered that the above and other objects of the present invention may be accomplished in the following manner. Specifically, it has now been discovered that an improved high energy propellant may be prepared that has an impetus value of at least 1300 J/g. This family of propellants is expected to be of great value in new versions of the M829 cartridge as well as for other future tank systems yet to be developed.

The propellant comprises an oxetane thermoplastic elastomer energetic binder admixed with a high energy explosive filler. An oxetane thermoplastic elastomer can be melted at moderate elevated temperature and then solidified into an elastomeric material once it is cooled to a lower temperature such as ambient or lower. It is made from two types of monomers: 3,3-bis-azidomethyl-oxetane, or BAMO as a hard block, and 3-azidomethyl-3-methyloxetane, or AMMO as a soft block. The oxetane thermoplastic elastomer energetic binder, or AMMO/BAMO, eliminates the need for solvents in processing. It is included as a binder in an amount suitable for processing and formulating the desired propellant. Preferred amounts range from about five percent to about thirty percent by weight, based on the total weight of the propellant.

The high energy explosive filler comprises from about seventy percent to about ninety-five percent by weight of the propellant. There are a number of preferred propellant fillers. is selected from the group consisting of Hexanitrohexaazaisowurtzitane or CL-20, 1,3,3-Trinitroazetidine or TNAZ, and the presently used RDX. Mixtures thereof are also contemplated, particularly in paired propellants as described below.

The preferred propellant of this invention may also include an explosive plasticizer, preferably in an amount of about four percent to about seven percent of the plasticizer by weight of the propellant. Examples of preferred plasticizers are 1,3,3-Trinitroazetidine or

TNAZ, Butane-trio-trinitrate or BTTN, Trimethylolethane Trinitrate or TMETN, Triethylene Glycol Dinitrate or TEGDN, Bis, 2,2 - Dinitro propyl acetal/Bis 2,2 - Diniro propyl formal or BDNPA/F, Methyl Nitrato ethyl nitramine or methyl NENA, ethyl NENA. These plasticizers may be used alone or in combination.

It has also been discovered that a pair of high energy propellants may be combined to produce a propellant mixture having a first propellant having a burning rate at least three times faster than the burning rate of the second propellant. In the preferred embodiment, the first propellant includes an oxetane thermoplastic elastomer energetic binder admixed with CL-20 high energy explosive filler. The second propellant including an oxetane thermoplastic elastomer energetic binder admixed with RDX high energy explosive filler or RDX and TNAZ mixtures. The ratio of burning rates may be varied from at least 2.0 times to as high as 4.8 times, or higher. Of course, plasticizers and relative amounts for each of the first and second propellants are within the same ranges as for the single propellants.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention has many advantages over the prior art propellant formulations. In its simplest form, the invention comprises an oxetane thermoplastic elastomer energetic binder admixed with a high energy explosive filler. A plasticizer may be added in some applications.

The oxetane thermoplastic elastomer energetic binder is an essential part of the invention, and is available from Thiokol Corporation. It is capable of being melted at elevated temperatures to allow the binder to be processable with other propellant ingredients without the use of solvents, and this is a major advantage. In addition, as will be shown below, the oxetane thermoplastic elastomer energetic binder has excellent mechanical properties that are superior to conventional propellants because of elastomeric characteristics, especially at cold temperatures such as -20° to -40° F. This binder also has good mechanical properties that are important for uniform ballistic performance as well as having low vulnerability to shaped charge jet impact.

In order to verify the excellent properties of the oxetane thermoplastic elastomer energetic binder, thermal stability tests were performed. Results of these tests are shown in Table I below.

TABLE I

Sample	Self Heat, $^{\circ}$C	Ignition, $^{\circ}$C
OXETANE Only	166	229
OXETANE/TNAZ (1:1)	153	216
OXETANE/CL-20 (1:1)	181	206
OXETANE/RDX (1:1)	196	222

In order to demonstrate the effectiveness of the propellants of this invention, a number of gun propellant formulations were mixed and extruded. The method of preparing the formulations comprised the

steps of mixing at about 95 $^{\circ}$C and extruding at slightly lower temperatures. Processing at these temperatures provided a safe operating margin of at least 50 $^{\circ}$C because the self heat temperatures of the filler ranges from about 175 $^{\circ}$C to 192 $^{\circ}$C, but the preferred plasticizer TNAZ melts around 100 $^{\circ}$C, so that as some of the TNAZ begins to melt during processing at 95 $^{\circ}$C, a more fluid mix results that is easier to process. Presented below in Table II are seven formulations that have been prepared. All values for the composition are given in percent by weight, based on the total weight.

TABLE II

Sample	Oxetane	Filler/amount	Impetus, J/g	Flame, $^{\circ}$K
A	24	CL-20/76	1297	3412
B	24	TNAZ/76	1309	3321
C	20	TNAZ/76*	1335	3475
D	20	CL-20/76*	1324	3575
E	13.3	RDX/80**	1319	3395
F	18	RDX/76***	1306	1348
G	20	CL-20****	1348	3683

* Sample also included 4 % BDNPA/F as plasticizer

** Sample also included 6.7 % BDNPA/F as plasticizer

*** Sample also included 6 % TNAZ as plasticizer

**** Sample also included 4% TNAZ as plasticizer.

Each of the above batches was formulated into a propellant by mixing and then extruding at a lower temperature. Selection and control of the precise extrusion parameters was important to obtain proper grain dimensions without excessive swelling or deformation. Table III below identifies the barrel temperature, die temperature and ram speed for each sample batch.

TABLE III

Sample	Barrel temp., °C	Die temp. °C	Ram speed, in/min.
A	82	70	0.14
B	95	86	0.14
C	89	82	0.06
D	87	78	0.03
E	100	91	0.14
F	100	85	0.08
G	66	55	0.04

Each of these formulations were tested for various properties to demonstrate the efficacy of the present invention. Specifically, impact, differential thermal analysis (DTA), and electrostatic and friction sensitivity characteristics. Presented below in Table IV are the results of these tests. The results show that impact sensitivities are similar to the conventional propellant M43, and that the products of this invention are quite thermally stable. A negative annotation for electrostatic sensitivity indicates no reaction to a 12 Joule electrostatic charge while a negative friction value is for a test with a 60 pound weight. The last two samples were not fully tested and n/a indicates that no data is available.

TABLE V

Sample	Impact (cm)	DTE,Self heat (°C)	DTA, Ignition (°C)	Electrostatic (12 Joules)	Friction (Bole)
A	50	179	203	neg	neg
B	40	175	211	neg	neg
C	20	175	212	neg	neg
D	40	174	206	neg	neg
E	40	206	225	neg	neg
F	n/a	n/a	n/a	neg	neg
G	n/a	n/a	n/a	neg	neg

The next evaluation of these samples was to determine the burn rate at various conditions. The data for the burn rates, presented

below in Table VI, represent closed bomb data. As can be seen, RDX containing samples E and F have the slowest burning rates, which is comparable to the LOVA type M43 formulations. The CL-20 samples A, D and G have much faster burn rates, the improvement being about 2.7 times at 10,000 psi and 4.8 at 25,000 psi. The TNAZ filled samples B and C have intermediate burning rates and sample G is the fastest. Based upon this data, a combination of a first propellant having burning ratios at least three times faster than a second combined propellant is now possible.

TABLE VI

Sample	10 kpsi (inch/sec)	15 kpsi (inch/sec)	25 kpsi (inch/sec)	Exponent	Friction (10^{-3})
A	4.5	6.9	11.8	1.04	0.30
B	3.1	4.7	7.9	1.02	0.25
C	3.5	5.1	8.4	0.97	0.46
D	4.5	6.8	11.2	0.98	0.54
E	1.7	2.6	4.4	1.03	0.14
F	1.7	2.7	4.5	1.04	0.12
G	4.6	9.0	21.0	1.65	0.001

To complete the evaluation of the samples, some mechanical behavior tests were performed, the results of which are below in Table VII. Tests were done on an Instron test machine at low strain.

TABLE VII

Sample	Stress, (psi)	% elong (@ max stress)	Modulus, (psi)	Fail Modulus, (psi)	Failure Mode
A	1780	36.7	7650	742	B
B	1260	26.2	8370	2480	B
C	412	22.8	3160	1280	B,P
D	641	30.4	3190	456	B,P
E	555	16.5	6220	2870	P,SC
F	1970	18.8	18,800	5760	P,S
G	1680	30.8	8860	2860	P

The symbols for the failure data in the last column of Table VII are as follows: B = barrel, P = pancake, SC = slight crumble, and S = split

The data shows that high energy gun propellants at an energy level of 1300 J/g can be formulated with an Oxetane binder in combination with high energy fillers. Desirable burning rates with burn rate differential by a factor of 3 or more can be obtained from these formulations.

While particular embodiments of the present invention have been illustrated and described herein, it is not intended that these illustrations and descriptions limit the invention. Changes and modifications may be made herein without departing from the scope and spirit of the following claims.